Characterisation of the Surface and Structural Properties of Gamma Ray and Electron Beam Irradiated Low Density Polyethylene

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Abstract

It is of vital importance that most medical devices are sterilised prior to use. However, sterilisation performed by ionising radiation can cause significant damage and degradation to polymers due to the energetic secondary electrons released from the primary irradiation event. In this present work, low density polyethylene (LDPE) was subjected to a commercial gamma irradiator and a high energy electron beam irradiator (combined 10/12MeV unit, 30KW). Characterisation was performed on the non-irradiated and irradiated LDPE samples by several analytical methods. X-ray diffraction (XRD) revealed that the percentage crystallinity and crystalline size had no significant alterations. Scanning electron microscope (SEM) imagery illustrated a rougher sample surface subsequent to electron beam irradiation at 400kGy which was perhaps attributed to oxidative degradation. In addition, the fracture behaviour of the cryofractured surface specimens was highly influenced by electron beam irradiation. Colorimetry was employed in quantifying the effects of electron beam and gamma ray processing on the colour changes of LDPE. This technique identified that the gamma ray process leads to more discolouration of the LDPE material, indicating that the electron beam process was more user friendly.

Keywords

Electron beam irradiation; gamma irradiation; crystallinity; contact angle; colour measurement; low density polyethylene

Introduction

Crosslinking of low density polyethylene (LDPE) without the addition of crosslinking agents or other special additives can be achieved by exposing the material to various forms of radiation such as electron beam and gamma ray (Sharif, Aziz, & Hashim, 2000). This has potential commercial use due to property improvements where 3D crosslink networks form between polymeric chains which in turn could enhance thermal and chemical resistance and mechanical characteristics. Radiation crosslinking results in a product with properties that are similar or identical to those obtained by the chemical crosslinking process (Chodák, 1998; Salovey, 1962; Yan, Luo, & Jiang, 1993). Radiation crosslinking occurs quickly, therefore producing higher throughput. Another advantage of this process consists of the possibility of generating active intermediates in the solid polymer within a large temperature interval (Khonakdar, Jafari, Wagenknecht, & Jehnichen, 2006). However, ionising irradiation can result in adverse effects on material properties by promoting degradation affects. Yet the balance of crosslinking and scission reactions in polyolefin chains exposed to radiation processes that produce free radicals can perhaps result in sought after properties and new applications (Smedberg, Hjertberg, & Gustafsson, 1997; Suarez, da Costa Monteiro, & Mano, 2002; Viksne, Zicans, Kalkis, & Bledzki, 1997). Radiation initiates scission of C-C and C-H bonds leading to the formation of alkyl radicals (Kurtz, 2004) which are required to form chemically crosslinked 3D structure of covalent bonds between adjacent chain molecules. In addition, these free radicals can result in recombination processes (Göschel & Ulrich, 2009). The alkyl and the allyl radicals are the predominant free radicals produced by radiation in polyethylene (Dole, 1972). Radicals are also the reason for discolouration in some materials. This is due to the radicals produced

by irradiation which react with the oxygen diffusing through the material causing bleaching of the radical based colour centres (Clough, Gillen, Malone, & Wallace, 1996). Temperature plays a significant role in radiation induced reactions as a rise in 10°C doubles the reaction rates, therefore when polyethylene is exposed to 1 kilogray, the temperature of the material increases by 0.43°C (Berejka & Cleland, 2011). A thorough description of the numerous initiation procedures along with the mechanisms for these processes and specific features of each procedure was given in comprehensive reviews from Bhattacharya (2000) and Lazar, Rado & Rychlý (1990).

The current investigation is focused on another strategy, not explored up until now to the best of our knowledge. This aims at quantifying the effects of electron beam (combined 10/12MeV unit, 30KW) and gamma ray processing on the colour changes of LDPE while utilising two commercial processes. In addition, the percentage crystallinity obtained in previous results by MDSC (Murray et al., 2012), was compared to the percentage crystallinity values obtained from the XRD characterisation technique. This identified the relationship between both processes and determined whether the values fall into a similar range. SEM was performed on the surface of the non-irradiated and irradiated LDPE material to determine surface modifications induced by irradiation. Finally, goniometry was conducted on the surface of the non-irradiated and irradiated LDPE material by the sessile drop method. This distinguished the effects of irradiation on the hydrophilicity of the material.

Experimental

Material

This study was conducted using virgin low density polyethylene manufactured by ExxonMobil Chemical Company (Houston, USA). The material was supplied by the National Chemical Company, Ireland. Melt flow index (MFI) of the material was 0.55g/10min under loading of 2.16kg at 190°C, while the density was 0.929g/cm^{3}and had a melt temperature of 114°C.

Injection moulding and packaging

An Arburg injection moulding machine was utilised in manufacturing type IV ASTM (American society for testing and materials) D638 testing specimens with the use of LDPE material. Sample preparation played a significant role in the electron beam process as this controlled the uniformity of the irradiation dose on the samples. Each of the samples i.e. tensile specimens, and impact bars were placed into sealable LDPE bags in order to contain them in a controlled environment. Sample size, density, weight and orientation remained identical for each bag during the packaging process to facilitate uniform irradiation (Murray et al., 2013b).

Electron beam irradiation

Firstly, dose mapping was conducted on the LDPE testing specimens to determine the maximum and minimum dose zones and process reproducibility. A Mevex high energy electron beam irradiator (combined 10/12MeV unit, 20KW) was used to irradiate the samples at doses of 25, 50, 75, 100, 150, 200 and 400kGy. The dose rate was approximately 12.5kGy per pass on each side to accomplish a uniform irradiation dose. All samples were irradiated at room temperature in the presence of air at the Synergy Health plant (Tullamore, Ireland). The non-irradiated samples served as the baseline for each of the results obtained from the characterisation techniques.

Gamma ray irradiation

Gamma radiation was carried out on the LDPE samples with dose rates of 25 and 200 kGy. In order to attain accurate results, the samples were packaged and labelled identically, according to the samples for electron beam processing. A commercial gamma irradiator using a cobalt 60 energy source was used at the Synergy Health facility, Westport, Co. Mayo. The process was also performed in an air atmosphere.

X-Ray Diffraction

X-ray diffraction of all batches was examined via a Bruker AXS D8 Discover X-ray diffractometer. This characterisation technique was employed to investigate the modifications induced by irradiation such as crystallite size and relative crystallinity. All samples were positioned onto the sample loading plate located in the XRD chamber. During setup, the loading plate was set to oscillation mode (x,y axis movement) with an amplitude of 0.5mm. The value of 2θ ranged from 5 to 35°. The GADDS and Eva software was used to analyse the recorded results. By implementing Bragg's law, the d-spacing was determined from the XRD pattern. The d-spacing that depends on the angular position theta can be derived from equation 1(Suryanarayana & Norton, 1998).

$$n\lambda = 2d\sin\theta \qquad \text{Equation 1}$$

Where: n = Reflection order (1,2,3....)

λ = X-Ray wavelength

d = d-spacing

θ = Diffraction angle

Results from the experiment was analysed and the crystalline size was derived from the following equation (Niemantsverdriet, 2007; L. Singh & Singh, 2004):

$$\chi = \frac{K\lambda}{\beta \cos\theta} x \frac{180}{\pi} \qquad \text{Equation 2}$$

Where:

k = Scherrer constant or shape factor (e.g. **0.94** for cubic particles)

λ = Wavelength

θ = Incident angle (Half the 2 theta value)

β = Peak width (°)

Scanning Electron Microscope (SEM)

Surface morphologies of the non-irradiated and irradiated LDPE samples were investigated with the aid of a SEM. All test specimens were placed on special sample holders and then sputter coated with gold using a Beltec SCD 005 sputter coater prior to testing. A Mira FE SEM was used in high vacuum mode with an acceleration voltage of 10kV, a resolution of 100μm and a magnification of 388 x. (Murray et al., 2013a)

Goniometry

The contact angle was measured while operating an FTA (First Ten Angstroms, Virginia) 1000 machine. Each sample was measured three times in the same order to obtain a consistent value while using the sessile drop method. For contact angle measurements, a 0.002ml droplet of distilled water was ejected out of the micrometer syringe (GS-1200) onto the sample while using a 27 gauge needle. Images of the droplet on the surface of the sample were taken over a period of approximately 20 seconds and the FTA software was used to investigate the outcome result.

Colorimetry

Yellowness index was carried out according to ASTM D 1925 using a Lovibond RT600 sphere spectrophotometric colorimeter. Calibration was conducted on the instrument prior to testing by means of a calibration unit that was provided with the equipment (L = 94.91, a -1.01, b = +0.09). Five tests were measured from each sample of the different dose ranges. Each test performed on the non-irradiated and irradiated (electron beam and gamma ray) PEBA samples provided values for Hunter L (black (0) to white (100)), Hunter a (green (-) to red (+)) and Hunter b (blue (-) to yellow (+)).The overall colour difference was established by implementing statistical analysis of the ΔE values for L, a, and b. ΔE was calculated by using the following formula (Perera, Albano, González, Silva, & Ichazo, 2004):

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \qquad \text{Equation 3}$$

ΔE is expressed as the difference between the control sample and the irradiated sample colour values.

Results and discussion

X-Ray Diffraction

To determine the effects of crosslinking on the crystalline structure and the degree of crystallinity of the irradiated LDPE material, XRD analysis was conducted. From the XRD pattern illustrated in Fig. 1, it is clear that the virgin material is semicrystalline in nature due to the peak at 21.65° (2θ) (R. Singh, Samra, Kumar, & Singh, 2008). The XRD patterns of various irradiated LDPE samples are presented in Fig. 1while the parameters are provided in Table 1. Three crystalline peaks appeared during this experiment at 21.5°, 24.3° and 36.5°. The orthorhombic phase for the peak located at 21.5° is 110, for peak 24.3° it is 200 and for peak 36.5° it is 210. These phases represent the diffraction angle which corresponds to the orthorhombic crystallite plane.

It is apparent that the peaks are not increasing according to the increase in irradiation dose as can be seen from the peak at a 2θ value of 21.5° in Fig. 1. The larger the crystals are of a given component, the sharper are the peaks on the XRD pattern for each crystal plane. As a result, the breadth of the peak can be related to the crystal size. The 150kGy sample had a remarkable increase in intensity at 21.5° from 793 (0kGy) to 1156.41 (150kGy). Scherrer equation (L. Singh & Singh, 2004) was utilised to calculate the crystalline size, whilst the GADDS software was employed to calculate the percentage crystallinity after the XRD experiment. Based on the results obtained in Table 1, it can be anticipated that upon irradiation there is only a slight change in both the percentage crystallinity and the crystalline size. This provides evidence that the electron beam irradiation mainly causes crosslinking to occur in the amorphous region

of the LDPE material. When the percentage crystallinity determined by XRD was compared to the percentage crystallinity of the MDSC experiment (Murray, et al., 2012), it was evident that the results were similar.

Scanning Electron Microscope (SEM)

In this study, four samples of the LDPE material were tested in order to identify changes induced by the electron beam irradiation process which are displayed in Fig. 2a-d. Two methods were implemented in order to discover these changes.

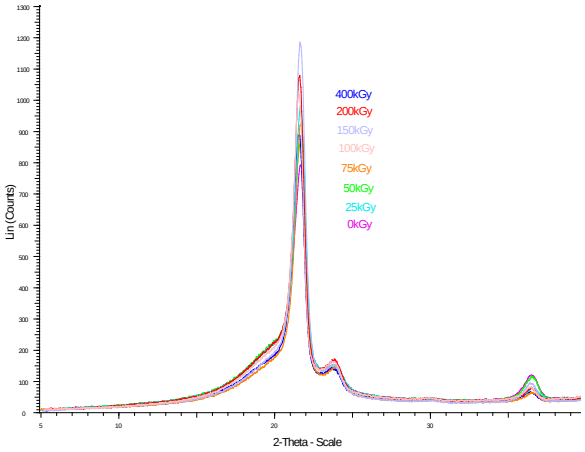

FIG. 1. XRD DIFFRACTOGRAM OF THE NON-IRRADIATED AND ELECTRON BEAM IRRADIATED LDPE IN THE 2Θ RANGE OF 5.2 - 40°

TABLE I XRD PARAMETERS OF THE NON-IRRADIATED AND ELECTRON BEAM IRRADIATED LDPE SAMPLES

Irradiation Dose (kGy)	2θ (deg.)	FWHM (deg.)	Crystallite Size L (Å)	XRD % Crystallinity	MDSC % Crystallinity
0	21.54	1.093	79	25.50	28.83
25	21.60	1.104	77	27.86	28.13
50	21.52	1.079	78	26.21	28.36
75	21.55	1.054	80	27.04	28.49
100	21.53	1.059	80	28.68	28.61
150	21.58	1.039	81	29.90	26.47
200	21.57	1.004	84	29.49	27.04
400	21.57	1.081	78	26.72	27.33

The first method involved testing the surface of the pristine (0kGy) and irradiated (400kGy) tensile specimens with an SEM at a magnification of 1.44kx. Before the test was conducted, each of the samples was placed on the pin mount adapter and then sputter coated in gold to enhance imagery during the experiment. The second method incorporated the investigation of freeze fractured (cryofracture) LDPE surfaces, before and after irradiation. This experiment included the testing of the 0 and 200kGy samples by use of SEM with a magnification of 388x. Previous to testing, the two samples (ASTM impact bars) were placed in liquid nitrogen for 20mins before being fractured by the charpy impact machine. LDPE is a flexible material by nature and would not break otherwise, thus liquid nitrogen was exploited to ensure that the polymer chains were completely frozen so as to achieve a high quality break. Both samples were left to one side after fracture, until they reached room temperature again. The samples were then prepared for SEM, by ensuring that the orientation of the fractured side was correctly placed on the pin mount adapter. Furthermore, they were sputter coated with gold to enhance imagery during the experiment. Surface changes (roughness changes) can be observed in a qualitative approach by the use of SEM imagery on each of the samples.

Image Fig. 2a (non-irradiated) displays a rough surface which appears to be blister like, while the irradiated (400kGy) sample at Fig.2 b demonstrates a smoother surface. This could be related to the formation of oxidation degradation on the surface of the LDPE material which in turn modifies the surface characteristics. In a previous study, Fourier transform infrared spectroscopy (FTIR) revealed that oxidative products were mainly found on the surface of LDPE (Murray, et al., 2012). Oxidative degradation caused by irradiation in air is a diffusion controlled process (Suarez & Mano, 2001), consequently, it affects mainly the surface layers and mechanical properties of irradiated polymers.

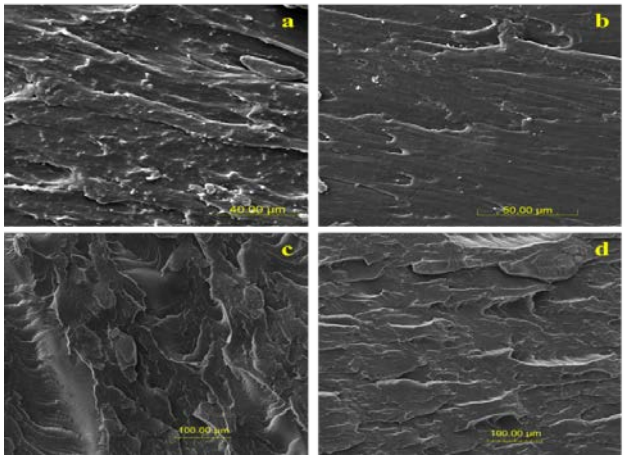

FIG. 2 (A) SEM IMAGE OF LDPE 0KGY AT 1.44KX FOR SURFACE OF TENSILE SPECIMEN (B) SEM IMAGE OF LDPE 400KGY AT 1.44KX FOR SURFACE OF TENSILE SPECIMEN (C) SEM IMAGE OF LDPE 0KGY AT 388X FOR SURFACE OF FRACTURED IMPACT BAR (D) SEM IMAGE OF LDPE 200KGY AT 388X FOR SURFACE OF FRACTURED IMPACT BAR

The effects of irradiation on the texture of the fractured surfaces are clearly defined by the images illustrated in Fig. 2c and d. Both samples can be characterised as a brittle fracture due to the glassy appearance and the presence of sharp fracture edges. A cleaner break is evident from image Fig. 2d which is perhaps due to the occurrence of crosslinking after irradiation exposure inducing fragility. The flaky/scaly appearance of both fractured samples could be attributed to damage caused by the intersection of microscopic crack branches with the main fractures produced during the impact (Carlos Miguez Suarez & Biasotto Mano, 2000; Lustiger & Corneliussen, 1987). Based on this study it was apparent that electron beam irradiation had a strong influence on the fracture behaviour. In addition, the surface characteristics were modified due to radiation degradation which is apparent from images a and b in Fig. 2.

Goniometry

The extent of hydrophilic modification of the electron beam radiation modified LDPE samples was investigated by contact angle measurements. Hydrophilicity gives a material a tendency to attract water to its surface, hence absorbing the water. The contact angle method used in this experiment was the sessile drop, which is the most widely used technique. Contact angle measurements were performed by calculating the angle formed between the surface of the solid and the line which was tangent to the droplet radius from the point of contact with the solid. When the contact angle has a value of zero, it results in wetting, whilst if the angle is between 0 and 90°, it results in the spreading of the water across the material surface. If the contact is between 0 and 90°, the material can be classified as hydrophilic due to the molecular attraction. However, if the contact angle is greater than 90°, the material can be classified as a hydrophobic material. This results in the water 'balling-up' hence, causing it to run of the surface easily (Dadbin, 2002; Garbassi, Morra, & Occhielo, 1996).

Fig. 3 illustrates the variation of the contact angle measurements of LDPE samples for different irradiation dose rates. Different values have been reported for the contact angle of untreated LDPE from the literature depending on the procedure and samples used. A value of 87° was given from research work which entailed modifying various polymers using low pressure plasma (Palmers, 2000). In this study a value of 94° was obtained for the non-irradiated LDPE after three measurements were carried out. The objective of this study was to compare the non-irradiated sample (baseline) with those of the irradiated samples ranging between 0 and 400kGy. As the irradiation dose increased the contact angle varied between 94° and 103°. The highest surface contact angle was observed at 150kGy and from 200 to 400 kGy the contact angle began to even out. Where the contact angle reduced, this could be attributed to the formation of hydrophilic groups such as polar species which were enhanced due to oxygen rather than the change of surface roughness (Abdul-Kader, Turos, Radwan, & Kelany, 2009; Sanchis, Blanes, Blanes, Garcia, & Balart, 2006). Hydrophilic group formation is a two-step process whereby the first step concentrates on the creation of free radicals on a polymer surface by electron beam irradiation. The second step involves interaction between free radicals in polymer chains and oxygen which results in the formation of polar groups such as carboxyl, carbonyl, hydroxyl and ester groups (Abdul-Kader, et al., 2009). Where the contact angle increased in the sample demonstrated in Fig. 3, the irradiation was causing the surface to become non-polar which in turn caused the material to repel the droplet of water (surface prefers neutral molecules). The variations throughout the graph could be attributed to the different exposure levels to oxygen during the irradiation process. Fig. 4 represents the images of the contact angles obtained for each of the non-irradiated and irradiated LDPE samples.

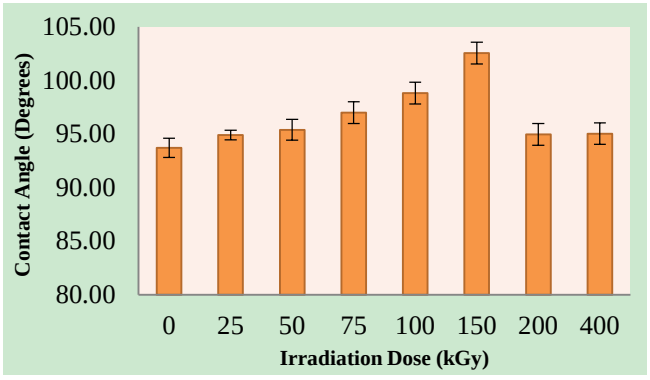

FIG. 3 VARIATION OF CONTACT ANGLE MEASUREMENTS OF LDPE AS A FUNCTION OF ELECTRON BEAM IRRADIATION DOSE

Colorimetry

Colorimetry measurements were conducted on the LDPE samples before and after irradiation with the gamma ray and electron beam processes. The exposure rate of the electron beam irradiated samples ranged between 0 and 400kGy, whilst the gamma

irradiated samples ranged between 0 and 200kGy in this experiment. The Hunter *b* value in Fig. 5 demonstrated a slight increase from -2.85 to 0.097 (400kGy) as the electron beam irradiation dose increased. This was more pronounced for the gamma irradiated samples as it increased from -2.85 to 2.01 (200kGy). Consequently, the gamma irradiated samples became more yellowish in colour. Fig. 7 displays an image of the samples after electron beam irradiation, which illustrates a slight change in colour which corresponds to the data obtained.

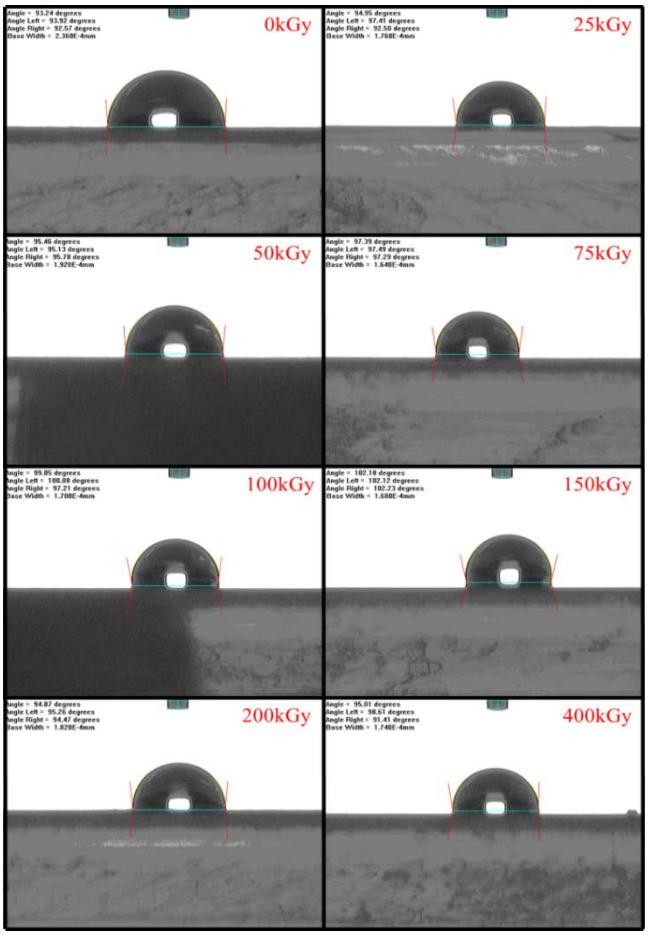

FIG. 4 CONTACT ANGLES REPRESENTING THE NON-IRRADIATED AND ELECTRON BEAM IRRADIATED LDPE SAMPLES

Fig. 6 demonstrated a slight increase for the electron beam irradiated samples with 2.94 being the overall difference as the irradiation dose increased. There was a significant increase observed for the *ΔE* value of the gamma irradiated samples with an overall difference of 14.59 as the irradiation dose increased. An explanation for such changes after the exposure of irradiation was perhaps due to the formation of conjugated double bonds and/or the entrapment of free radicals (Perera, et al., 2004). Overall, this study suggested that low density polyethylene was more sensitive to gamma ray processing in contrast to electron beam processing. This was perhaps due to the longer exposure times of irradiation during the gamma ray process.

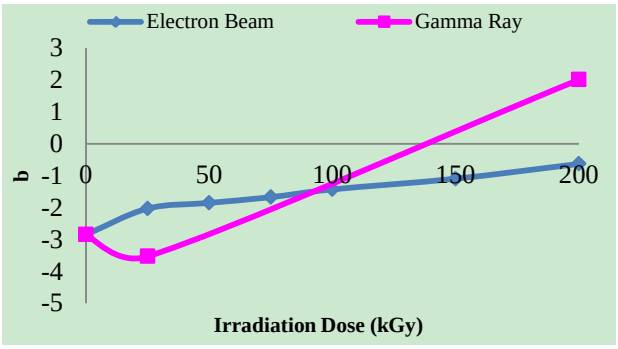

FIG. 5 HUNTER *B* VALUE FOR LDPE VS. IRRADIATION DOSE

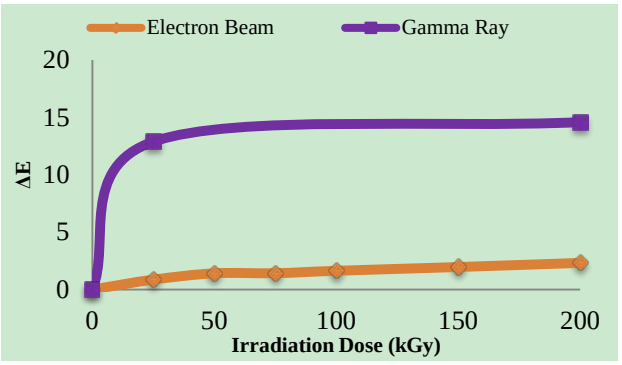

FIG. 6 HUNTER *ΔE* VALUE FOR LDPE VS. IRRADIATION DOSE

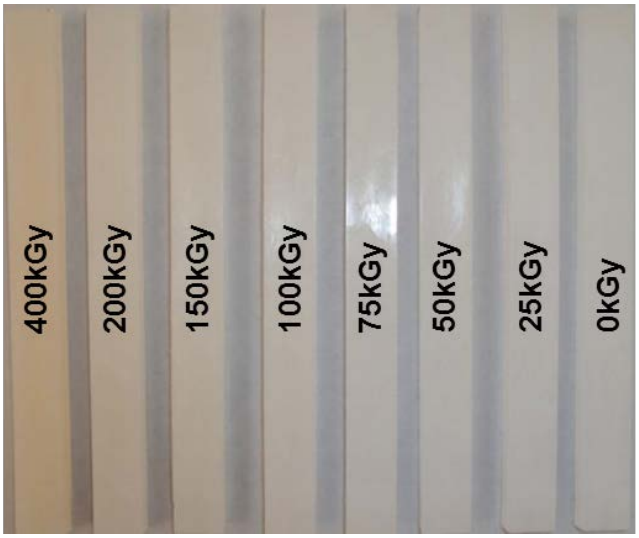

FIG. 7 COLOUR CHANGE OF LDPE BEFORE AND AFTER ELECTRON BEAM IRRADIATION

Conclusion

Despite the impossibility of getting a very accurate description of the fine details of the structure of the amorphous component, a few striking results have been obtained from the present refinements. X-ray diffraction studies implied that radiation crosslinking

occurred without significantly affecting the material crystalline structure and degree of crystallinity. The results obtained from this experiment correlated very well with the results obtained in the MDSC experiment. With regards to SEM imagery, a considerable amount of degradation transpired on the surface of the material subsequent to electron beam irradiation which could be attributed to oxidation. In addition, it was apparent from the freeze fractured samples that the fracture behaviour was influenced by electron beam irradiation. Contact angle analyses illustrated that the hydrophilic/hydrophobic characteristics of the surface functional groups varied according to different irradiation dose ranges. Irradiation resulted in the differing of surface tension values which perhaps came about from oxidation during the electron beam irradiation process. Colorimetry revealed that both the electron beam and gamma ray processes cause modifications to occur in the colour of the material. This characterisation technique aided in quantifying the discolouration for both processes and from this experiment it was evidently shown that gamma irradiation was the most detrimental method of the two.

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